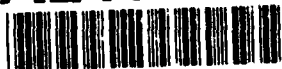


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OFFICE OF NAVAL RESEARCH

Grant N00014-90-J-1193

TECHNICAL REPORT No. 69

Frequency Dependence of Two-Photon Resonances and Damping in Polymers

by

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Prepared for publication

in

*Synthetic Metals*

Departments of Chemistry and Physics  
Washington State University  
Pullman, WA 99164-1046

December 1991

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91-17252



# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited	
b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
PERFORMING ORGANIZATION REPORT NUMBER(S) WSU/DC/91/TR-69		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics Washington State University	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION	
c. ADDRESS (City, State, and ZIP Code) 428 French Administration Building Pullman, WA 99164-1046		7b. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	
a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Grant N00014-90-J-1193	
c. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
1. TITLE (Include Security Classification) Frequency Dependence of Two-Photon Resonances and Damping in Polymers			
2. PERSONAL AUTHOR(S) X. Sun, K. Nasu, C. Wu, L. Li, D. L. Lin and Thomas F. George			
3a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) December 1991	15. PAGE COUNT 12
16. SUPPLEMENTARY NOTATION Prepared for publication in <u>Synthetic Metals</u>			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	POLYMERS	
		FREQUENCY DEPENDENCE	
		DAMPING	
		THIRD-HARMONIC GENERATION	
9. ABSTRACT (Continue on reverse if necessary and identify by block number)			
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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson		22b. TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL

## Frequency Dependence of Two-Photon Resonances and Damping in Polymers

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### Abstract

For the two-photon resonance in the third-harmonic generation (THG) spectrum of trans-polyacetylene, the existing theories can only qualitatively rather than quantitatively explain the experimental data. In this paper a damping mechanism is proposed. It shows that once the excitation-dependent damping is taken into account, the whole experimental spectrum of the THG can be quantitatively interpreted by our theoretical calculations.



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## 1. Introduction

There are two distinct peaks in the spectrum of the third-harmonic generation (THG) of trans-polyacetylene (PA), one at 0.6 eV and another at 0.9 eV [1]. How to give a quantitative explanation of this frequency dependence is a focus of the optical nonlinearity study in polymers. Many theories have been proposed to interpret the physical mechanism of this resonance structure [2-12]. The first peak at 0.6 eV has been well understood within the origin of the three-photon resonance. As for the second peak at 0.9 eV, qualitatively it is commonly realized that it is produced by the two-photon resonance. However, none of the existing theories can quantitatively account for the experimental data.

Wu first proposed an analytic theory for the nonlinear optical susceptibility of the polymers by using the Keldysh Green function and starting from a non-interacting electron model [2]. The significance is that this theory requires no adjustable parameters. It rigorously gives a divergence at one third of the optical gap  $E_g$  and a cusp at one half of  $E_g$ . The positions of the divergence and the cusp agree well with the experimental peaks. However, it has been pointed that the cusp is seriously suppressed by the damping, and the remaining bump is too small to explain the second peak [9].

Soos and his co-workers presented a correlated electron theory for the optical nonlinearity of polymers based on the Hubbard and Pariser-Parr-Pople (PPP) models [3-6]. Their calculations show that the single-strand PPP results give the two-photon resonance at  $0.75E_g$ , and the interchain interactions in PA significantly shifts the two-photon resonance to the red. It qualitatively explains the THG spectra of PA and other polymers, but it is difficult to get quantitative agreement with the experiments.

Dixit, Guo and Mazumdar advanced the essential-states mechanism [8]. They found that there is only one two-photon state, called an  $mA$  state, which dominates the THG spectrum, and the level of this state is always bounded by  $1B$  and  $2B$ . Since the energy difference between  $1B$  and  $2B$  vanishes when the chain length increases infinitely, the  $mA$  state approaches  $1B$  in the limit of  $N \rightarrow \infty$ . Based on these features, they inferred that the two-photon resonance is exactly at  $E_g/2$ . Their findings about this dominant state are substantial to understanding the underlying physics of the resonance structure. However, the final inference about the position of the two-photon resonance is not true. The problem is that the state  $mA$  is only associated with  $1B$ . When the length becomes very long,  $2B$  is very close to  $1B$  and the oscillator strength of the transition  $1A \rightarrow 2B$  is comparable with that of  $1A \rightarrow 1B$ . Then the transitions from  $2B$  to various  $A$  should be considered, and there can exist another dominant two-photon state  $m'A$  associated with  $2B$ . The  $m'A$  level will be higher than  $2B$ . Therefore,

in the case of a very long chain, it cannot be guaranteed that the peak of the overall two-photon process is still bounded between  $1B$  and  $2B$ . More directly, this inference can be verified by the Peierls-Hückel model, which is soluble and can offer an unambiguous answer. We have provided an analytic expression of the THG spectrum for the Peierls-Hückel model [10], which rigorously shows that the peak of the two-photon resonance is near  $0.6E_g$  rather than  $0.5E_g$ , so that the dominant states cannot lead to the inference that the two-photon resonance is exactly at  $E_g/2$ .

From the above analyses it is seen that the two-photon resonance in polymers has not been well understood, where the various theoretical results for the position of the two-photon resonance peak are higher than the experimental data. This paper presents a simple damping mechanism to solve this problem. It shows that once the excitation-dependent damping is considered, the position of the two-photon resonance peak will shift to  $0.5E_g$ , and the theoretical result of the whole THG spectrum will well agree with the experimental data.

## **2. Excitation-Dependent Damping**

Due to the interaction between the electrons and phonons and defects in the polymer, the excited states must possess some damping. Since the higher excited state has more channels to decay, the damping is dependent on the excitation. The higher is the excited state, the

larger is the damping. For the excitation-dependent damping, as we shall discuss below, its role in the resonance phenomenon is not just to eliminate the divergence. However, both the non-interacting and the correlated theories of the optical nonlinearity do not carefully consider the damping, which is the reason why the existing theories cannot fully explain the THG spectrum of PA.

Before making our quantitative calculation, it is instructive to give a physical explanation as to why the excitation-dependent damping can shift the two-photon resonance peak to the red side. Without the excitation-dependent damping, the top of the two-photon resonance is near  $0.6E_g$ , as shown by the dashed line in Figure 1. Since the right wing of this peak has higher excited energy than the left wing, the damping suffered by the right wing will be larger than that by the left wing. Then, after taking the excitation-dependent damping into account, the right wing of the two-photon resonance peak is suppressed more than the left wing. So the top of the two-photon resonance peak is shifted toward the left side.

For the Peierls-Hückel model we have

$$H = - \sum_{n,s} [t_0 + (-1)^{n+1} \Delta/2] (C_{n+1,s}^\dagger C_{n,s} + \text{h.c.}) \quad , \quad (1)$$

where  $C_{n,s}^\dagger$  creates an electron of spin  $s$  at site  $n$ ,  $t_0$  is the one-electron hopping integral, and  $\Delta$  is the gap parameter. The analytic expression for the third-order nonlinear susceptibility is [10]

$$\chi^{(3)}(\omega) = \chi_0^{(3)} (5\pi/1024N\delta) \Sigma [A(x,z)+B(x,z)] , \quad (2)$$

where

$$\chi_0^{(3)} = 4e^4\sigma(2t_0a)^3/45\pi\Delta^6, \quad \delta = \Delta/2t_0 , \quad (3)$$

$$\begin{aligned} A(x,z) = & (1/x^9) \{ [5-8x^2(1+\delta^2) + 20\delta^2x^4]/(x^2-z^2) \\ & + [2048(x^2-1)(1-\delta^2x^2)]/[x^2-(2z)^2] \\ & + [19683-1749x^2(1+\delta^2)+15228\delta^2x^4]/[x^2-(3z)^2] \} , \end{aligned} \quad (4)$$

$$\begin{aligned} B(x,z) = & (24/x^9) \{ 7[7-6x^2(1+\delta^2)+5\delta^2x^4]/(x^2-z^2) \\ & - 14(x^2-1)(1-\delta^2x^2)x^2/(x^2-z^2)^2 \\ & + 5x^2[5-4x^2(1+\delta^2)+3\delta^2x^4]/(x^2-z^2)^2 \\ & - 20x^4(x^2-1)(1-\delta^2x^2)/(x^2-z^2)^3 \\ & - 61[7-6x^2(1+\delta^2)+5\delta^2x^4]/[x^2-(2z)^2] \\ & + 122x^2(x^2-1)(1-\delta^2x^2)/[x^2-(2z)^2]^2 \\ & - 27[7-6x^2(1+\delta^2)+5\delta^2x^4]/[x^2-(3z)^2] \\ & + 54x^2(x^2-1)(1-\delta^2x^2)/[x^2-(3z)^2]^2 \} , \end{aligned} \quad (5)$$

$$x = [\epsilon_C(k) - \epsilon_V(k)]/2\Delta + i\eta , \quad z = \hbar\omega/2\Delta , \quad (6)$$

$\epsilon_C(k)$  and  $\epsilon_V(k)$  are the energies of conduction and valence bands,  $\eta$  the damping,  $a$  the lattice constant, and  $\sigma$  the number of chains in one unit of cross-section. For trans-polyacetylene, the bandwidth  $4t_0 = 10$  eV, the optical gap  $2\Delta = 1.8$  eV,  $\delta = 0.18$ , and  $\sigma = 3.2 \times 10^{14} \text{ cm}^{-2}$ .

Since the main contribution comes from the low-lying excited states, which are near the bottom edge of the conduction band  $k_0 = \pi/2a$ , the damping  $\eta(k)$  of the low-lying excited states can be expanded about  $k_0$ , where only the leading term is important. Then,



phenomenologically, the excitation-dependent damping can be expressed as

$$\eta(k) = \alpha a(k_0 - k) \quad . \quad (7)$$

Since the average damping is about few percent of the gap, the numerical factor  $\alpha$  is about 0.5. Equation (7) shows that the higher excited state, which has bigger momentum deviation  $(k_0 - k)$ , possesses larger damping. As has been explained, this feature has the significance of shifting the two-photon resonance peak to the red side.

### 3. Results and Discussion

The whole THG spectrum of trans-polyacetylene can be obtained by substituting the damping (7) into Eq. (2). Since the length  $N$  of different chains in the polymer can be different, we must take an average over some length distribution  $W(N)$ . One commonly-used distribution is

$$W(N) = (1-P)^2 N P^{N-1}, \quad N = 1, 2, \dots \quad (8)$$

The numerical result for the average length  $N = 200$  is shown by the solid line in Fig. 1, where the dots represent the experimental data. For comparison, the THG spectrum without the excitation-dependent damping is also presented by the dashed line in Fig. 1. Both the solid and dashed lines have two peaks: the first one sits at  $E_g/3$ ,

which is the three-photon resonance and the second peak sits around 0.5 and  $0.6E_g$ , respectively. This figure clearly shows the important effect of the excitation-dependent damping. Before considering this damping, the top of the two-photon resonance peak is found at  $0.6E_g$ . It is the excitation-dependent damping that shifts the top from 0.6 to  $0.5E_g$ . The solid line agrees very well with the experimental data. Therefore, we conclude that the damping is an important mechanism to understanding the optical nonlinearity of the polymer.

In this paper we have introduced the excitation-dependent damping into the imaginary part of the excitation energy. While this is only a phenomenological theory, it is possible to develop a microscopic damping theory. Starting from the electron-phonon interaction, the excitation-dependent damping can be calculated by means of the Green function.

We would like to thank Dr. K. Iwano and Dr. Z. Shuai for helpful discussions. This work was partially supported by Project 863, the National Natural Science Foundation of China and the U.S. Office of Naval Research.

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**Figure Caption**

Figure 1. THG spectrum of trans-polyacetylene. The solid and dashed lines are the theoretical results with and without the excitation-dependent damping, respectively. The dots are the experimental data.

